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QUANTITATIVE PHASE ANALYSIS OF DEVONIAN SHALES BY COMPUTER
CONTROLLED X-RAY DIFFRACTION OF SPRAY DRIED SAMPLES.

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ABSTRACT

Spray drying is shown to be an effective and rapid method for preparing samples for quantitative analysis by x-ray powder diffraction. Previously intractable problems like the simultaneous analysis of multiple phases in orientation prone systems can be carried out. Using this method, and a computer controlled diffractometer, five and six phase analyses of Devonian shales can be accomplished in approximately forty minutes. A rapid and convenient method for using the absorption diffraction technique for x-ray quantitative analysis is described.

INTRODUCTION

X-ray powder diffraction is the principal tool used for the quantitative analysis of crystalline phases in mixtures. In spite of its wide spread use, the unreliability of intensity measurements, principally due to preferred orientation, continues to severely limit its application. Quantitative analyses of orientation prone materials, like the clay minerals, have been the cause of a considerable number of studies over the years. The methods arising from these studies usually involve the preparation of a large number of reference patterns of oriented specimens along with tedious and problematic particle size separations (1-2).

Spray drying powders to form spherical shaped agglomerates has been shown to minimize preferred orientation (3). This technique should allow x-ray quantitative analysis of previously intractable systems. This study was undertaken for two reasons. One was to establish a rapid and routine method for quantitative phase analysis as part of a large scale project for characterizing the eastern United States Devonian oil and gas bearing shales. The second reason was to evaluate the effectiveness of spray drying as a general sample preparation technique for use in the quantitative analysis of orientation prone materials. The complex clay containing Devonian shales are well suited to this purpose.

Experimental

To assess the validity, accuracy and precision of quantitative analysis using spray dried samples, two mixtures of minerals were prepared. One was a 60-40 weight percent mixture of kaolinite and quartz. The other was a mixture of illite, quartz, feldspar and chlorite in proportions similar to that found in the Devonian shales. In addition the procedure to be described was applied to 29 samples of shales from West Virginia and New York State.

Since full chemical analysis of each of the shales to be analyzed was available, from other work being done in conjunction with this study, the x-ray absorption coefficients could be calculated. This permitted the use of the Diffraction Absorption Technique of Analysis (4-5) based on the relationship:

$$\text{weight fraction of phase } j = \frac{I_{hkl \text{ } j \text{ mixture}} \left(\frac{\mu}{\rho} \right)_{j \text{ mixture}}}{I_{hkl \text{ } j \text{ pure}} \left(\frac{\mu}{\rho} \right)_{j \text{ pure}}}$$

This equation has been applied in a number of studies where authors usually determine $(\mu/\rho)_{\text{mixture}}$ by direct measurement. Most of these studies have commented on the errors introduced by both orientation efforts and the errors in measuring (μ/ρ) . Both of these sources of error should be minimal in this study.

Qualitative analysis by x-ray powder diffraction showed that the shales typically contain as principal phases: illite,

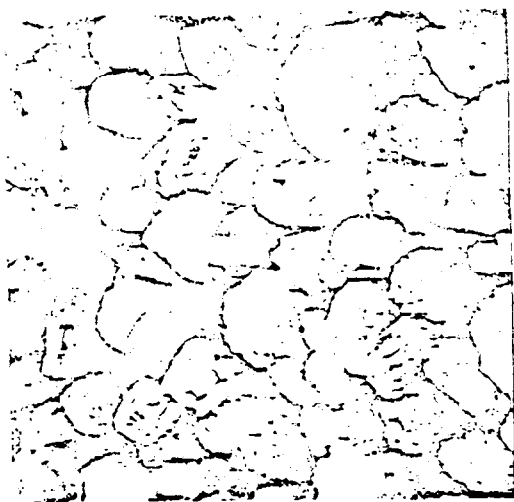


Fig. 1. Spray dried ripidolite before fine grinding (200X)



Fig. 2. Spray dried ripidolite before fine grinding (1200X)

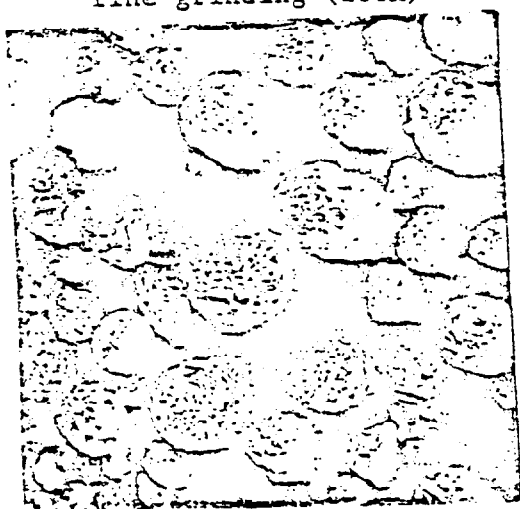


Fig. 3. Spray dried ripidolite after fine grinding (200X)



Fig. 4. Spray dried illite (640X)

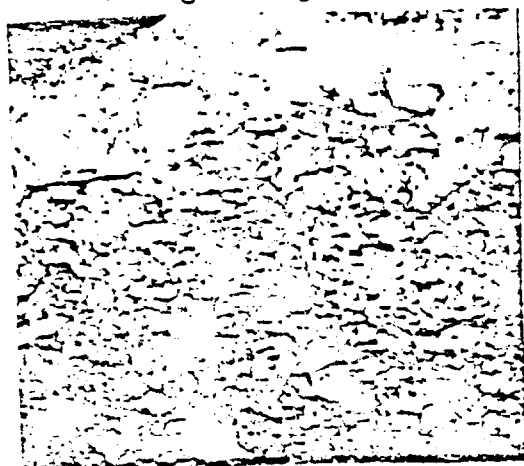


Fig. 5. Middlesex shale before spray drying (200X)



Fig. 6. Middlesex shale after spray drying (720X)

quartz, feldspar, chlorite or kaolinite, pyrite and sometimes siderite. In order to obtain the intensities of lines in the pure materials, our mineral collection was surveyed. The sample of each mineral with diffraction pattern closest to the patterns found in the shales was selected as a standard. Due to the high degree of peak overlap in the shale powder patterns, integrated intensities could not be obtained so background corrected peak heights were used. In order to avoid redetermining the standards before each analysis, a method was devised which eliminated day to day variations in incident beam intensity and line voltage instabilities in the detector system. This method involved the fabrication, from brass, of an x-ray diffractometer powder sample holder with a narrower than usual sample chamber. A constant portion of this sample holder was in the x-ray beam during each analysis. Brass was chosen because it had a non-overlapped line at $49.075^\circ 2\theta$ and because its other lines did not obscure those to be used in the mineral analyses. The ratio of the intensity of the analysis line of each mineral standard to that of brass was then determined. Table 1 gives the 2θ angles used for counting the peaks and background for each material. Using typical count rates for illite, a major phase, we calculated (6) that counting times of 300 seconds on peaks and 100 seconds on background would produce results with counting errors on the order of 1 percent. These times were used to measure the intensity ratios given in Table 1. The standard deviations were computed from counting statistics.

All analyses were carried out using a Norelco Vertical diffractometer with a diffracted beam graphite monochromator using Cu K α radiation. The diffractometer had a 1° divergence slit and a 0.003" recieving slit. It was aligned for high resolution such that the K α_1 - K α_2 doublet would resolve at $28^\circ 2\theta$, and therefore relatively low count rates were observed. The scintillation detector and a 2θ controlling stepping motor were connected to a Camberra interface which was controlled by a PDP 11 minicomputer. The computer is configured with 56 K bytes of memory and two floppy disk drives.

Computer Controlled Analysis

A computer program was written in FORTRAN IV for the PDP 11 using the RT 11 operating system. The program is interactive, requesting operating parameters from the user. Routine information, which will not normally change from run to run, is stored on a disk file. In fact, Table 1 is a listing of this file. With the exception of the first record for brass, each record on the file contains the information necessary for the computer to measure and compute the weight percent of a particular mineral

TABLE 1.
Data File for Computer Controlled Shale Analysis

	Bkg Angle	Peak Angle	μ/ρ	$\frac{I \text{ Standard}}{I \text{ Brass}}$	σ
Brass	51.800	49.075	[100.]	[300.]	
Illite	17.000	19.840	43.0	1.070	0.087
Quartz	17.000	20.875	34.4	7.200	0.330
Feldspar	28.900	27.950	37.9	5.740	0.510
Chlorite	13.200	12.515	94.2	1.630	0.240
Pyrite	33.600	33.085	191.0	2.400	0.500
Kaolin	11.400	12.380	30.0	2.775	0.041
Siderite	28.900	32.100	154.0	2.580	0.140

phase in any unknown sample. The first record provides the peak and background angles for the brass line and the background and peak counting times in seconds to be used in the analysis of each phase (these have been placed in brackets).

The program has two modes of operation. The first mode is to measure data for a new standard and add this to the existing file, or create a new file if one does not exist. In this mode the diffractometer is directed to oscillate, a user specified number of times, between determination of the background corrected intensity for the brass peak and the peak chosen for the new standard. When finished an average value for $I \text{ standard}/I \text{ brass}$ is computed along with its standard deviation. These values with the other information in Table 1 are then added to the end of the computer file. As new phases were encountered in the shales a run of a pure standard mineral in this mode would update the file and permit its analysis in any future specimen.

The second mode of operation is the normal analysis mode. Here the computer directs the movement of the detector to the 2 θ position of the brass peak, found in the first record on the file and counts for 300 sec. Then the detector is positioned to count background and the corrected brass intensity is computed. Next the record corresponding to the first of the mineral phases to be analyzed is read and the intensities are measured. The mineral to brass intensity ratio is then calculated. Finally this value is converted into a weight percent using the mass absorption coefficient and the intensity ratio of the pure phase also found on the file. The analysis result for this phase is printed on the operators console and analysis of

Table 2. Sample run of quantitative analysis computer program.

AUTOMATED QUANTITATIVE ANALYSIS USING
THE INTENSITY RATIO METHOD. VER 6

ENTER CURRENT TWO-THETA VALUE: 4.0

ENTER MU ON RHO FOR THIS SPECIMEN: 48.5

ENTER TITLE FOR RUN:
MIDDLESEX SHALE 10 AM APRIL 20

IS THIS A NORMAL RUN? (ENTER A ZERO) OR A LOOP RUN OR STANDARD?
(ENTER NUMBER OF LOOPS):

0

DO YOU WANT THE REF. PEAK DETERMINED ONLY ONCE? (ENTER 0), OR
BEFORE EACH UNK PEAK? (ENTER 1):

0

HOW MANY STANDARDS DO YOU WANT TO DETERMINE?

LISTING OF STANDARDS = (-1)

USE ALL STANDARDS IN RUN = (0)

SPECIFIC NUMBER OF SIDS = (#): 5

ENTER THE NUMBER OF STANDARDS TO BE RUN: 2,3,4,5,6

MOUNT THE SPECIMEN IN THE DIFFRACTOMETER.
WHEN READY; HIT RETURN

ANALYSIS RESULTS FOR-MIDDLESEX SHALE 10 AM APR 20

NAME	PEAK-CNT	BKG	NET-CPS	SIGMA	RATIO	SIGMA	CONC	SIGMA
BRASS	38174.	1402.	113.23	0.75				
ILLITE	22862.	1946.	56.75	0.67	0.50	0.01	52.83	4.30
QUARTZ	63861.	1992.	192.94	0.95	1.58	0.02	31.03	1.42
FELDSPAR	15343.	2230.	28.84	0.63	0.23	0.01	5.15	0.46
CHLORITE	17318.	2394.	33.79	0.66	0.26	0.01	8.18	1.20
PYRITE	9675.	2280.	9.45	0.58	0.07	0.00	0.72	0.15

TOTAL 97.91 +, - 7.53

ANOTHER SAMPLE FOR THESE STANDARDS? YES = (0); NO = (1): 1

ANOTHER NEW SAMPLE? YES = (0); NO = (1): 1

EXIT

the next phase is begun. An example run of this mode of operation is shown in Table 2. The underlined items are the user's response to the questions asked by the program. This example requested that standards 2 through 6 (as given in Table 1) be analyzed. This five-phase determination was then carried out with no further user intervention in approximately forty minutes.

Materials

Illite: this mica-like clay mineral has a variable composition due to extensive solid solution. Our illite standard material was purified from a sample of the American Petroleum Institute reference clay No. 36 (7) obtained from Wards (3). This illite found at Morris Illinois contains quartz as the major impurity and probably a trace of kaolinite. Preparation of this material involved grinding, suspension in an aqueous medium (about 10% by weight illite) with Calgon added as a deflocculant. After 24 hours of settling, the top part of the solution was withdrawn, centrifuged and dried. This purified material, which was subsequently spray dried, contained only a trace of quartz, with a total impurity level of probably 3%. Chemical analysis showed Si = 21.76%, Al 12.98%, Fe 2.88%, Mg 1.49%, Ca 0.42%, P 0.47%, Ti 0.50%, Na 0.25%, K 3.24%. The most intense peak free from serious overlap was chosen for analysis of each phase. For spray dried illite this was the 111 line near 4.46Å. It is interesting to note that this line is more intense than the basal (001) reflection when the specimen is spray dried.

Quartz: a pure sample of < 200 mesh was ground for one hour and spray dried. Since the most intense quartz line interferes with the illite 003 we chose the second most intense line at 4.26Å for analysis.

Feldspar: a sample of oligoclase from Mitchell County, North Carolina was closest in diffraction pattern to the shale feldspars. This material was analyzed as Si 23.80%, Al 12.38%, Fe 0.27%, Ca 3.44%, Na 6.25%, K 0.42%. The sample was ground to < 325 mesh and spray dried. The most intense line near 3.20Å was chosen for analysis.

Chlorite: a sample of ripidolite was used as a standard for this platy disilicate material. A Wards sample from Goscheneralpe Switzerland was ground to < 325 mesh and spray dried. Chemical analysis showed Si 11.5%, Al 10.96%, Fe 24.06%, Mg 6.03%, Ti 0.02%. The 002 line near 12.5° was used for analysis.

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Pyrite: a Wards sample from Rico, Colorado was ground to <325 mesh and spray dried. The 200 line which is the most intense peak in both the calculated and spray dried patterns was used. The powder Diffraction File pattern (6-710) incorrectly lists the 311 as the 100% line.

Kaolinite: the sample, kaolex D-6, a Georgia kaolin from the J. M. Huber Corp (9) was sufficiently fine to be spray dried directly. The particle size is reported (9) as being 62-68% < 2 μ m and 12-15% >5 μ m. The most intense line, 002 near 12.4 $^{\circ}$ was chosen for analysis. This line is in the same location as the line used for chlorite. We were forced to use these conflicting lines because of their high relative intensities and the low concentration of these two minerals. To differentiate chlorite from kaolinite, oriented slides of non-spray dried shales were prepared and treated with DMSO (10). The analysis of these diffraction patterns showed that when chlorite was present kaolin was not and when kaolin was present there were only trace amounts of chlorite. Thus with the introduction of a small amount of error the 12.4 $^{\circ}$ line was measured using either the chlorite or kaolin standard depending on the result of the DMSO test.

Siderite: a Wards sample from Roxsbury Connecticut was ground to <325 mesh and spray dried. This sample contained about 5% quartz which was ignored. The 104 reflection was used in the analysis.

Shales: the shales of unknown composition were broken into pieces of about 5 cm and ground first in a roll crusher. Representative samples were obtained using a riffle-type splitter. A 15g sample was then ground to <325 mesh in a spex mill or mortar and spray dried. Mass absorption coefficients were obtained by calculation from the known chemical analysis.

Two Phase Test Mixture: a 60% kaolinite 40% quartz mixture was weighed ground together and spray dried. The mass absorption coefficient was calculated as 31.8.

Four Phase Test Mixture: a mixture of 47.2% illite, 34.1% quartz 11.4% oligoclase and 7.3% ripidolite was weighed, ground and spray dried. These proportions are similar to those found in the shales. The mass absorption coefficient was calculated to be 45.0.

Results and Discussion

Figure 1 is a scanning electron micrograph of ripidolite which had been ground to <325 mesh and spray dried. This is a

good illustration of the sphere distorting effects of too large a ratio of crystallite size to agglomerate size. Figure 2 shows a close up of one of these agglomerates, clearly indicating the controlling effect which relatively large crystallites have on the microstructure of the sphere. After regrounding the ripidolite powder for 40 more minutes and spray drying, the spherical agglomerates shown in Fig. 3 were obtained. The finest particle size material we had available was the illite powder obtained by Stokes Law settling. On spray drying this powder, the smooth elliptically distorted spheres shown in Fig. 4 were obtained. The spray drying of the finely ground shales, such as the Middlesex, NY shale shown in Fig. 5 presents no special problems. The spray dried shale shown in Fig. 6 formed reasonably spherical agglomerates with no evidence of either orientation or particle segregation.

The quantitative analysis of the prepared kaolin-quartz mixture averaged over three computer runs of approximately one half hour each gave:

	Measured	Actual
Kaolin	57.7% \pm 4.1	60.0%
Quartz	41.3% \pm 3.6	40.0%

The analysis results for the prepared mixture of minerals with proportions similar to those found in Devonian shales are:

	Measured	Prepared
Illite	45.1% \pm 1.0	47.2%
Quartz	31.1% \pm 1.9	34.1%
Feldspar	11.6% \pm 1.7	11.4
Chlorite	7.4% \pm 0.6	7.3

These data were also averaged over three computer runs of approximately 40 minutes each.

These results show accuracy and precision typical of quantitative x-ray powder diffraction analyses on synthetic materials. Quantitative mineral analyses are often only reported to the nearest five percent. On considering such factors as the mineral nature of these materials, that analyses are made from a single pure standard and the numerous sources of error in the method of analysis, these results are impressive. They further confirm

the validity and desirability of spray drying as a preparation procedure for quantitative analysis.

The quantitative analysis, of the five or six phases identified in the 29 Devonian shales, summed to give a total analyzed mineral content between 90% and 105%. A typical computer run on the Middlesex NY shale shown in Figs. 5 and 6 is given in Table 2. The second from last column at the end of this table gives the concentration of the phase in weight percent. These runs usually take the computer about forty minutes to carry out.

Since the results on the synthetic samples show deviations of as much as 3% and the total mineral analysis of the shales vary over a 15% range, some consideration of the sources of error is in order. First let's consider errors in the general procedure not related to the mineral nature of the samples. The problems of microabsorption and of the peak counting method are well established and have some effect in our procedure. A more serious problem which arises only with spray dried samples is the tendency of our agglomerates to roll. This problem gets more serious at high angles where the sample holder angle is significant. The rolling of the specimen introduces a sample displacement error which will significantly shift a peaks position. Particularly when using the peak counting method this can introduce significant errors. This effect can be controlled by two methods. One is to spray a clear amorphous lacquer over the sample in the holder to keep it in place. The other is to add a peak location routine into the computer algorithm to find the top of the peak before counting. The traditional errors due to orientation and sample inhomogeneity appear not to be significant in this method.

The principal source of error in our analyses of the shales is the difference between the mineral phase found in the shale and that used as a standard. A number of serious assumptions have to be made in selecting standards. The extremely solid solution prone chlorites, feldspars, illites and siderite found in the Devonian shales showed considerable variation in their diffraction patterns. For example the choice of oligoclase as our feldspar standard does not imply that plagioclase and the alkali feldspars were not also present. In addition to this large error source the presence of impurity phases in our standards and the presence of small amounts of kaolinite in the chlorite shales and vice versa introduced more error. In general the shales show a high background with numerous unidentifiable small peaks; relative changes in these under the peaks to be analysed, is another source of error. On considering all of these difficulties the variations in the shale analyses seem reasonable. A more accurate analysis can be performed on any

one shale by a careful matching of standards to the mineral phases. For the survey we are conducting this improvement would not justify the extra time required.

CONCLUSION

Spray drying has been shown to be a simple and effective method for minimizing orientation effects for quantitative x-ray diffraction analysis. Use of this technique provides a method for the previous intractable problem of simultaneous multiphase analysis in orientation prone materials. The complex mixtures found in Devonian shales can be analyzed by this method.

ACKNOWLEDGMENTS

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